

Alkali Atoms Attached to ^3He Nanodroplets

R. Mayol*, F. Ancilotto[†], M. Barranco*, O. Bünermann[‡],
M. Pi*, and F. Stienkemeier[‡]

**Departament ECM, Facultat de Física.*

Universitat de Barcelona, E-08028 Barcelona, Spain.

*[†]INFM (Udr Padova and DEMOCRITOS National Simulation Center, Trieste);
Dipartimento di Fisica “G. Galilei”, Università di Padova I-35131 Padova, Italy*

[‡]Fakultät für Physik, Universität Bielefeld, D-33615 Bielefeld, Germany

We have experimentally studied the electronic $3p \leftarrow 3s$ excitation of Na atoms attached to ^3He droplets by means of laser-induced fluorescence as well as beam depletion spectroscopy. From the similarities of the spectra (width/shift of absorption lines) with these of Na on ^4He droplets, we conclude that sodium atoms reside in a “dimple” on the droplet surface and that superfluid-related effects are negligible. The experimental results are supported by Density Functional calculations at zero temperature, which confirm the surface location of Na, K and Rb atoms on ^3He droplets. In the case of Na, the calculated shift of the excitation spectra for the two isotopes is in good agreement with the experimental data.

PACS 68.10.-m, 68.45.-v, 68.45.Gd

1. INTRODUCTION

Detection of laser-induced fluorescence (LIF) and beam depletion (BD) signals upon laser excitation provides a sensitive spectroscopic technique to investigate electronic transitions of chromophores attached to ^4He droplets.¹ While most of atomic and molecular dopants submerge in helium, alkali atoms (and alkaline earth atoms to some extent²) have been found to reside on the surface of ^4He droplets, as evidenced by the much narrower and less shifted spectra when compared to those found in bulk liquid ^4He .^{3,4,5,6} This result has been confirmed by Density Functional (DF)⁷ and Path Integral Monte Carlo (PIMC)⁸ calculations, which predict surface binding energies

of a few Kelvin, in agreement with the measurements of detachment energy thresholds using the free atomic emissions.⁹ The surface of liquid ^4He is only slightly perturbed by the presence of the impurity, which produces a “dimple” on the underlying liquid. The study of these states can thus provide useful information on surface properties of He nanodroplets complementary to that supplied by molecular-beam scattering experiments.^{10,11} Hence, alkalis on the surface of helium droplets are ideal probes to investigate the liquid–vacuum interface as well as droplet surface excitations.

Microscopic calculations of ^3He droplets are scarce.^{12,13} The properties of ^3He droplets doped with some inert atoms and molecular impurities have been addressed within the Finite Range Density Functional (FRDF) theory,¹⁴ that has proven to be a valuable alternative to Monte Carlo methods which are notoriously difficult to apply to Fermi systems. Indeed, a quite accurate description of the properties of inhomogeneous liquid ^4He at zero temperature (T) has been obtained within DF theory,¹⁵ and a similar approach has followed for ^3He (see Ref. 14 and Refs. therein).

2. RESULTS

The experiments we report have been performed in a helium droplet machine used earlier for LIF and BD studies, and is described elsewhere.² Briefly, helium gas is expanded under supersonic conditions from a cold nozzle forming a beam of droplets traveling freely under high vacuum conditions. The droplets are doped downstream employing the pick-up technique: in a heated scattering cell, bulk sodium is evaporated in such a way that, on average, a single metal atom is carried by each droplet. Since electronic excitation of alkali-doped helium droplets is eventually followed by desorption of the chromophore, BD spectra can be registered by a Langmuir-Taylor surface ionization detector.¹⁶ Phase-sensitive detection with respect to the chopped laser or droplet beam was used. For that reason the BD signal (cf. Fig. 1), i.e. a decrease in intensity, is directly recorded as a positive yield. For these experiments, a new droplet source was built to provide the necessary lower nozzle temperatures to condense ^3He droplets.

For the spectroscopic measurements presented in the following, we have set the source pressure to 20 bar and the nozzle temperature to 11 K for ^3He , and to 15 K for ^4He . These conditions are expected to result in comparable mean cluster sizes around 5000 atoms per droplet.^{17,11} In Fig. 1 the absorption spectrum of Na atoms attached to ^3He nanodroplets is shown in comparison to Na-doped ^4He droplets.

The outcome of the spectrum of Na attached to ^3He nanodroplets is very

Alkali Atoms Attached to ^3He Nanodroplets

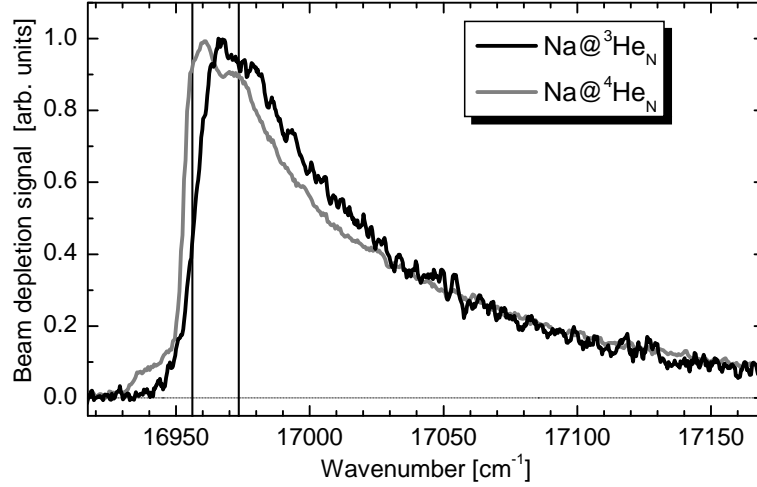


Fig. 1. Beam depletion spectra of Na atoms attached to $^3\text{He}/^4\text{He}$ nanodroplets. The vertical lines indicate the positions of the two fine structure components of the Na gas-phase $3p \leftarrow 3s$ transition.

similar to the spectrum on ^4He droplets. The asymmetrically broadened line is almost unshifted with respect to the gas-phase absorption. This absence of a shift immediately confirms the surface location because atoms embedded in bulk superfluid helium are known to evolve large blue-shifts of the order of a couple of hundreds of wavenumbers and much more broadened absorption lines.¹⁸ A blue shift is a consequence of the repulsion of the helium environment against the spatially enlarged electronic distribution of the excited state (“bubble effect”). The interaction towards the ^3He droplets appears to be slightly enhanced, evidenced by the small extra blue shift of the spectrum compared to the ^4He spectrum. In a simple picture this means that more helium atoms are contributing or, in other words, a more prominent “dimple” interacts with the chromophore. The upper halves of the spectra are almost identical, when shifting the ^3He spectrum by $7.5 \pm 1 \text{ cm}^{-1}$ to lower frequencies.

FRDF calculations at $T = 0$ confirm the picture emerging from the measurements, i.e. the surface location of Na on ^3He nanodroplets causing a more pronounced “dimple” than in ^4He droplets. We have investigated the stable configurations of an alkali atom on both ^3He and ^4He clusters of different sizes. The FRDF’s used for ^3He and ^4He are described in Refs. 19 and 20. The large number of ^3He atoms we are considering allows to use the extended Thomas-Fermi approximation.²¹ The presence of the foreign impurity is modeled by a suitable potential obtained by folding the helium density with an alkali-He pair potential. We have used the poten-

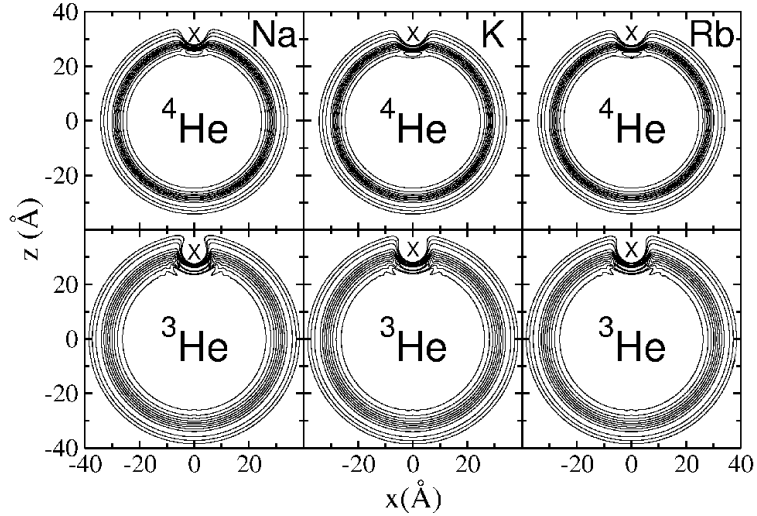


Fig. 2. Equidensity lines in the $x - z$ plane showing the stable state of an alkali atom (cross) on a He_{2000} droplet. The 9 inner lines correspond to densities $0.9\rho_0$ to $0.1\rho_0$, and the 3 outer lines to $10^{-2}\rho_0$, $10^{-3}\rho_0$, and $10^{-4}\rho_0$ ($\rho_0 = 0.0163 \text{ \AA}^{-3}$ for ^3He , and 0.0218 \AA^{-3} for ^4He).

tials proposed by Patil²² to describe the impurity-He interactions. Fig. 2 shows the equilibrium configuration for alkali atoms adsorbed onto He_{2000} clusters. Comparison with the stable state on the $^4\text{He}_{2000}$ cluster shows that, in agreement with the experimental findings presented before, the “dimple” structure is more pronounced in the case of ^3He , and that the alkali impurity lies *inside* the surface region for ^3He and *outside* the surface region for ^4He (the surface region is usually defined as that comprised between the radii at which $\rho = 0.1\rho_0$ and $\rho = 0.9\rho_0$, where ρ_0 is the He saturation density^{10,11,21}). This is due to the lower surface tension of ^3He as compared to that of ^4He , which also makes the surface thickness of bulk liquid and droplets larger for ^3He than for ^4He .^{10,11}

The deformation of the surface upon alkali adsorption is characterized by the “dimple” depth, ξ , defined as the difference between the position of the dividing surface at $\rho \sim \rho_0/2$, with and without impurity, respectively.⁷ For ^3He we have found $\xi \sim 4.4$, ~ 4.1 , and $\sim 4.3 \text{ \AA}$, for Na, K and Rb, respectively. The corresponding values for ^4He are $\xi \sim 2.3$, ~ 2.3 , and $\sim 2.0 \text{ \AA}$, respectively.

Solvation energies defined as $S_{Ak} = E(\text{Ak}@\text{He}_N) - E(\text{He}_N)$ have also been calculated and are shown in Fig. 3. The value $S_{Na} \sim -12 \text{ K}$ has been obtained within FRDF theory for Na adsorbed on the *planar* surface of ^4He

Alkali Atoms Attached to ^3He Nanodroplets

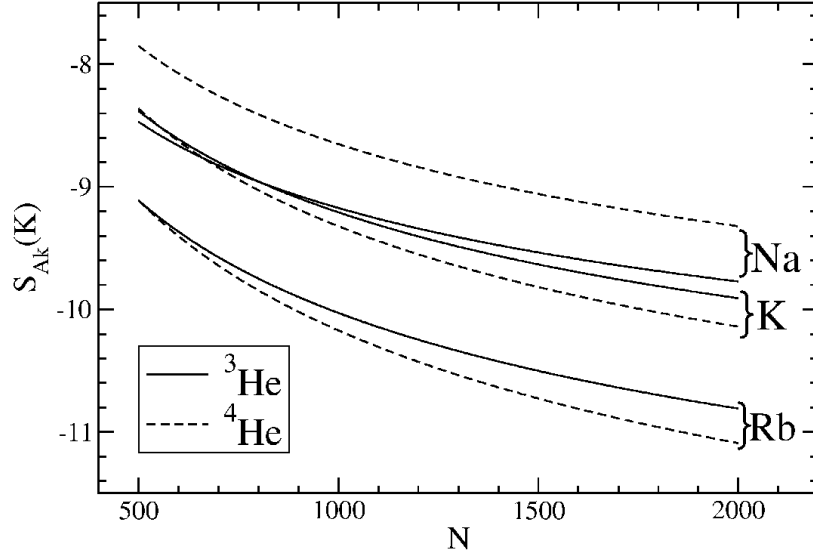


Fig. 3. Solvation energies as a function of the number of atoms in the droplet.

(Ref. 7), which corresponds to the $N = \infty$ limit. A detailed discussion on solvation energies and AkHe-exciplex formation on helium nanodroplets will be presented elsewhere.

Finally, we have obtained the shift between the ^3He and ^4He spectra in Fig. 1 within the Frank-Condon approximation, i.e. assuming that the “dimple” shape does not change during the Na excitation. The shift is calculated within the model given in Ref. 23, evaluating Eq. 6 therein, both for ^3He and ^4He . We have used the excited state A $^2\Pi$ and B $^2\Sigma$ potentials of Ref. 8 because their Na-He ground state potential is very similar to the Patil potential we have used to obtain the equilibrium configurations. For $N = 2000$, we find that the ^3He spectrum is blue-shifted with respect to the ^4He one by 6.4 cm^{-1} , in good agreement with the experimental value of $7.5 \pm 1\text{ cm}^{-1}$ as extracted from Fig. 1.

Our results thus show that alkali adsorption on ^3He droplets occurs in very much the same way as in the case of ^4He , i.e., the adatom is located on the surface, though in a slightly more pronounced “dimple”. The similarities in the experimental spectra are certainly remarkable for two apparently very different fluids, one normal and the other superfluid, and clearly indicate that superfluidity does not play any substantial role in the processes described here (we recall that while ^4He droplets, which are detected at an experimental T of $\sim 0.38\text{ K}$, are superfluid, these containing only ^3He atoms, even

R. Mayol *et al.*

though detected at a lower T of ~ 0.15 K, do not exhibit superfluidity²⁴). This is likely a consequence of the very fast time scale characterizing the Na electronic excitation compared to that required by the He fluid to readjust. The excitation occurs in a “frozen” environment and the only significant difference between ^3He and ^4He is due to the different structure of the “dimple”, which accounts for the small shift in their spectra observed in the experiments and found in our calculations as well.

ACKNOWLEDGMENTS

We thank Flavio Toigo for useful comments. This work has been supported by grants MIUR-COFIN 2001 (Italy), BFM2002-01868 from DGI (Spain), and 2001SGR-00064 from Generalitat of Catalunya as well as the DFG (Germany).

REFERENCES

1. F. Stienkemeier and A.F. Vilesov, J. Chem. Phys. **115**, 10119 (2001).
2. F. Stienkemeier, F. Meier, and H. O. Lutz, J. Chem. Phys. **107**, 10816 (1997); Eur. Phys. J. D **9**, 313 (1999).
3. F. Stienkemeier et al., Z. Phys. D **38**, 253 (1996).
4. F. Stienkemeier et al., J. Chem. Phys. **102**, 615 (1995);
5. C. Callegari et al., J. Phys. Chem. **102**, 95 (1998).
6. F. Brühl, R. Trasca, and W. Ernst, J. Chem. Phys. **115**, 10220 (2001).
7. F. Ancilotto et al., Z. Phys. B **98**, 323 (1995).
8. A. Nakayama and K. Yamashita, J. Chem. Phys. **114**, 780 (2001).
9. J. Reho et al., Faraday Discuss **108**, 161 (1997).
10. F. Dalfovo, J. Harms, and J.P. Toennies, Phys. Rev. B **58**, 3341 (1998).
11. J. Harms et al., Phys. Rev. B **63**, 184513 (2001).
12. V.R. Pandharipande, S.C. Pieper, and R.B. Wiringa, Phys. Rev. B **34**, 4571 (1986).
13. R. Guardiola, Phys. Rev. B **62**, 3416 (2000).
14. F. Garcias et al., J. Chem. Phys. **108**, 9102 (1998); *ibid.* **115**, 10154 (2001).
15. F. Dalfovo et al., Phys. Rev. B **52**, 1193 (1995).
16. F. Stienkemeier et al., Rev. Sci. Instr. **71**, 3480 (2000).
17. J. Harms and J. P. Toennies, unpublished results.
18. Y. Takahashi et al., Phys. Rev. Lett. **71**, 1035 (1993).
19. M. Barranco et al., Phys. Rev. B **56**, 8997 (1997).
20. R. Mayol et al., Phys. Rev. Lett. **87**, 145301 (2001).
21. S. Stringari and J. Treiner, J. Chem. Phys. **87**, 5021 (1987).
22. S.H. Patil, J. Chem. Phys. **94**, 8089 (1991).
23. S.I. Kanorsky al., Phys. Rev. B **50**, 6296 (1994).
24. S. Grebenev, J.P. Toennies, and A.F. Vilesov, Science **279**, 2083 (1998).